

REMARKS/ARGUMENTS

In view of the foregoing amendments and following remarks, favorable reconsideration of the pending claims is requested.

Status of the Claims

Claims 1-4, 6-8, 10 and 11 are pending.

Claims 5, 9, and 12-13 have been cancelled.

By way of this amendment, Claim 1 is amended to recite that the electrolytic solution comprises one electropolymerizable monomer and one source of protons. Claim 1 has further been amended to recite that the Bronsted acids are chosen from water and weak acids, and that that source of protons is present in an amount of between 50 and 10 000 ppm with respect to the total amount of the constituents of the said electrolytic solution.

Claim 1 has also been amended to clarify that the electrolytic solution is free of an electrochemical initiator.

Support for the Bronsted acids can be found on § [0042], for example, of the Application as filed.

With respect to the absence of an electrochemical initiator, Applicant respectfully submits that this amendment is implicitly supported by the specification as filed. In particular, the electrolytic solutions described in the Examples do not include electrochemical initiator. Indeed, one of ordinary skill in the art upon reading and understanding the examples would recognize that the inventive process does not use electrolytic solutions having an electrochemical initiator. Further, in the present invention the electrolytic solution comprises no oxidizing electrochemical initiator as it concerns anionic polymerization. In this regard, see the Rule § 1.132 Declaration of Dr. Deniau (attached), paragraphs 4-5. In particular, one of skill in the art pertaining to anionic polymerization would understand that an electrolytic solution anionic polymerization would not include an oxidizing electrochemical initiator. Thus, it can be readily seen that the amendments to claim 1 are fully supported by the specification as filed.

Claim 2 has been amended to consistent with the amendments to Claim 1.

Prior Art Rejections - 35 USC §103

Claims 1-4, 6-8, and 10 have been rejected under 35 U.S.C. § 103(a) as being unpatentable over U.S. Patent No. 3,554,882 to Hodes et al. Claim 11 has been rejected under 35 U.S.C. § 103(a) as being unpatentable over Hodes in view of U.S. Patent No. 6,375,821 to Jerome et al.

Applicant respectfully traverses the rejections.

In order to establish a *prima facie* case of obviousness, the cited art must disclose or suggest each and every claim element. If a single element is missing from the cited reference or combination of references, the claim is not obvious in view of the cited art. In the present case, the claimed invention is neither disclosed nor suggested by Hodes et al., or the combination of Hodes et al. and Jerome et al., and therefore the claimed invention is patentable over the cited art.

At the outset, Applicant submits that the process described in Hodes et al. is completely different than the claimed invention, and that the claimed invention provides surprising results cannot be predicted based on the teachings of Hodes et al. In this regard, the Applicant has provided a Rule § 1.132 Declaration of Dr. Deniau (attached). As set forth in paragraph 1 and the attached *curriculum vitae*, it can be seen that Dr. Deniau has significant experience in the present technological field and can therefore be considered an expert.

In paragraphs 3-5 of his Declaration, Dr. Deniau explains the significant differences between the claimed invention and the teachings of Hodes et al. In particular, Dr. Deniau emphasize that Hodes et al. must have an electrochemical initiator and that the process described in Hodes et al. only proceeds via radical polymerization in the presence of the initiator.

In sharp contrast, the claimed process does not include an electrochemical initiator because the monomer adsorbs on the surface of the cathode and is directly reduced in a radical anion, which then reacts by addition of a monomer. This results in growth of the grafted chains via anionic polymerization. However, Dr. Deniau further elaborates in paragraph 6 that the skilled worker specialized in anionic polymerization would know and have expected that the anionic extremity would have been killed by the addition of protons. In this regard, Dr. Deniau has cited to C. Bureau, Journal of Electroanalytical Chemistry, 1999, 479, 43 (attached). Based

on this understanding, Dr. Deniau concludes the man of skill in the art would not have added protons to the medium.

In paragraph 7, Dr. Deniau then explains that they have surprisingly shown that the addition of protons under specific conditions can allow anionic polymerization to develop and, surprisingly, to control film thickness.

Further, Hodes et al. does not teach a process in which a weak acid or water is used as the proton source. Quite to the contrary, Dr. Deniau explains in paragraph 8 that the teachings of Hodes et al. would lead one of skill in the art to used a highly acidic solution. As noted by Dr. Deniau, Hodes et al. specifically states that a pH of less 3 is desirable for the most rapid polymerization. In contrast to Hodes et al., the claimed invention uses only a low quantity of Bronset acid, (i.e., between 50-10,000 ppm) and as such, there is only fractions of H⁺ in the electrolytic solution. This is in stark comparison to the teachings of Hodes et al.

In paragraph 9, Dr. Deniau further elaborates that the claimed range of 50-10,000 ppm of water or weak acids is critical and that this criticality is shown in the Examples of the instant application. In this regard, Dr. Deniau describes in detail how the examples show the criticality of the claimed range of 50-10,000 ppm. Thus, it can be seen that the claimed invention is significantly different than the process of Hodes et al., and in fact provides improvements that are unexpected and surprising in view of what one of ordinary skill in the art would expect. Accordingly, the claimed invention is patentable over the cited art. Withdrawal of the rejections is requested.

In view of the foregoing amendments and discussion along with the attached Declaration of Dr. Deniau, Applicant submits that the prior art rejections have been overcome and that the invention as claimed does fulfil non-obviousness criterion with respect to the cited prior art, and that its patentability is completely demonstrated.

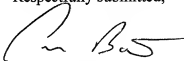
Accordingly, for all of the foregoing reasons, the Applicant requires the withdrawal of the rejection under 35 USC § 103 and the allowance of Claims 1-4, 6-8 and 10-11.

It is not believed that extensions of time or fees for net addition of claims are required, beyond those that may otherwise be provided for in documents accompanying this paper. However, in the event that additional extensions of time are necessary to allow consideration of this paper, such extensions are hereby petitioned under 37 CFR § 1.136(a), and any fee required

Appl. No.: 10/573,947
Amdt. dated 11/10/2011
Reply to Office action of 07/21/2011

therefore (including fees for net addition of claims) is hereby authorized to be charged to Deposit Account No. 16-0605.

Respectfully submitted,



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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

IN RE APPLICATION OF:

Christophe BUREAU *et al.*

SERIAL No.: 10/573,947

: GROUP ART UNIT: 1723

FILED: April 17, 2007

: EXAMINER: LEADER, WILLIAM T

FOR: METHOD FOR FORMING A POLYMER FILM ON A SURFACE THAT
CONDUCTS OR SEMICONDUCTS ELECTRICITY BY MEANS OF
ELECTROGRAFTING, SURFACES OBTAINED, AND APPLICATIONS THEREOF

DECLARATION UNDER 37 C.F.R. § 1.132

COMMISSIONER FOR PATENTS
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ALEXANDRIA, VIRGINIA 22313-1450

SIR:

I, G. DENIAU, do hereby declare and state the following:

1. I am a Doctor of applied chemistry (Paris University), Researcher in CEA (Commissariat à l'Energie Atomique), since the 1st March 1990.
Enclosed, please find a copy of my *curriculum vitae* and a list of scientific publications, which clearly indicate my expertise in the electropolymerisation field.
2. I am the main Inventor of the above-captioned patent application ("the '947 Application") and therefore I am very familiar with the subject application. I have read and understood the Final Office Action issued by the U. S. Patent and Trademark Office on July 21, 2011. It is my understanding that the Examiner has rejected Claims 1-4, 6-8 and 10 of "the '947 Application" under 35 USC §103 as being unpatentable over Hodes *et al.* and Claim 11 as being unpatentable over Hodes *et al.* in view of Jerome *et al.*

3. Regarding the US Patent 3,554,882 of Hodes *et al.*, it appears that this document concerns the deposition of a thick and adherent polymer coating on a metallic cathode from a solution containing a solvent in which a polymerizable monomer, a strong acid and an electrochemical initiator are soluble.

More particularly, Hodes *et al.* describe at column 2, lines 20 to 35 a water solution (10 mL) containing 10 wt% of acrylamide, 1 wt% of N,N'-methylenebisacrylamide, 2 wt% of N,N'-ethylenebisacrylamide, 0.5 mL of concentrated HCl and 0.5 mL of H_2O_2 (at 3%).

The Examiner indicates that concentrated HCl contains 38% of hydrogen chloride (Condensed Chemical Dictionary, pp. 486-487), and that an amount of 0.5 mL of 38% hydrogen chloride in 10 mL of water corresponds to approximately 19 000 ppm.

4. Contrary to the process of the invention, the method described by Hodes *et al.* only works via radical polymerisation in the presence of an electrochemical initiator, i.e. H_2O_2 in the example. **The presence of an electrochemical initiator is compulsory** in Hodes *et al.* Said electrochemical initiator is an oxidative species which, after protonation in acidic medium, gives a fragment bearing a net positive charge. Upon electrolysis, this positive fragment drifts to the cathode where it is reduced to form a neutral radical ($\text{HO}\cdot$) which initiates the vinyl polymerization. Therefore, in Hodes *et al.* the polymerization is indirect as it is not directly initiated on the surface of the electrode.

The mechanism of this initiation scheme is described col. 2, beginning line 39 of Hodes *et al.*

5. In the present invention, the electrolytic solution implemented in the claimed process comprises no oxidizing electrochemical initiator. The monomer adsorbs on the surface of the cathode is directly reduced in a radical anion ($\text{R}\cdot^-$). Such radical is unstable at the cathode (electrostatic repulsion) but his short life time nevertheless allows the grafting on the surface of the cathode. The anionic extremity of the radical then reacts by addition of a monomer, and the growth of the grafted chains takes place by anionic polymerisation.
6. The skilled worker specialized in anionic polymerization knows that such an anionic extremity will be killed by protons, and the chain growth interrupted because of protons (see the paper by C. Bureau, Journal of Electroanalytical Chemistry, 1999, 479, 43).

For these reasons, the man skilled in the art would never have added protons to the medium.

7. In spite of these prejudices, my team and I have shown that the addition of protons in specific conditions can allow anionic polymerisation to develop and, surprisingly, even improve the control of the film thickness.
8. Therefore, another fundamental difference is the high content of protons implemented in Hodes *et al.* as the use of strong acids like HCl leads to a widely superior quantity rather than the 50-10 000 ppm claimed range.

Besides, it is explicitly mentioned col. 2, l. 4-8 of Hodes *et al.* that: "A highly acidic solution is required for rapid polymerization. For a specific composition, the amount of acid used for the most rapid polymerization must be adjusted. A pH of less than 3 is desirable for the most rapid polymerization".

Therefore, this teaching would not have motivated the man skilled in the art to limit the protons content, but on the contrary it would rather have encouraged increasing the protons content higher.

In the invention, only a few quantity of Bronsted acid, *i.e.* coming from water or weak acids, is added which means that there is only fractions of H^+ in the electrolytic solution.

The adjustment of the water quantity in the process of the invention allows the control of the electrografted polymer on the electrode by controlling the polymerisation reaction of the anionic end-groups, whereas in Hodes *et al.* the use of a strong acid impacts on the quantity of positively charged species which, after reduction, will initiate and accelerate the radical polymerisation.

9. Page 3 of the Final Office Action, the Examiner considers the concentration of HCl as a controlled parameter in the process of Hodes *et al.*, and thus is recognized as a result-effective.

The Examiner also adds that the choice of HCl would have been a matter of routine optimization within the skill of the ordinary worker in the art, and that differences in concentration will not support the patentability of subject matter encompassed by the prior art ***unless there is evidence indicating such concentration is critical.***

On this point, my team and I have demonstrated in an unambiguous manner in the Examples of the Application the **critical effect** of the claimed range 50-10 000 ppm of water or weak acids:

- Example 1, Figure 2 shows that the thickness of electro-grafted films passes through a maximum for an intermediate water content (which is closed to 800 ppm), before decreasing and disappearing for very high water contents;
- Example 4 and Figure 4 illustrate the fact that the curves giving the thickness as a function of the protons content are curves which pass through a maximum lower than 10 000 ppm. These results demonstrate the existence of a water content of greater than 50 ppm for which the thickness obtained is greater than that accessible under anhydrous conditions. It is observed that the slopes of the curves are, in absolute value, lower above this concentration than below: it is with control of the protons content above this concentration, and not below, that it is possible to achieve good control with regard to the thicknesses of the films obtained;
- Example 5 and corresponding Figure 5 demonstrate that according to the support electrolyte the protons content of the medium can be adjusted to the value of the maximum of the thickness/protons content curves and that it is possible to have available solutions which decrease in hygroscopicity, and thus increase in stability,

as this protons content increased. It appears from Figure 5, which represents the thickness of the films obtained as a function of the protons content, that the thickness of the electro-grafted films is maximal for protons content going from 400 to approximately 1 000 ppm.

10. As Hodes *et al.* relates to radical polymerisation rather than anionic polymerisation, and as there is no teaching, suggestion or motivation in this document to develop a process for the polymerisation of a polymer film on a cathodic electrically conducting or semiconducting surface using a specific content of protons (50-10 000 ppm) coming from water or weak acids, without implementing electrochemical initiator, such specific features improving considerably, the control of the electrografted film thickness, the process as claimed does fulfil the non-obviousness criterion.
11. The undersigned petitioner declares further that all statements made herein of his own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were with the knowledge that wilful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such wilful false statements may jeopardize the validity of this Application or any Patent issuing thereon.



Signature

October 20 2011

Date

Encl.: - Curriculum vitae and list of publications,
- Copy of the publication of C. Bureau, Journal of Electroanalytical Chemistry, 1999, 479, 43.

Date of birth : 04/06/59
CEA enter date : 01/03/1990.....
Center : Saclay



DENIAU GUY



Appointment: DSM/Saclay/IRAMIS/SPCSI/LCSI
Position title : Research engineer

Competences

Controlled fields of competences

- Fundamental and applied research in surfaces and interfaces chemistry
- Research valorization
- Multipartners contracts responsibility
- PhD management

Career path

Dates	Appointment	Position title and memorable feature	under the responsibility of...
Current position	Surfaces and interfaces research engineer, under the responsibility of S. Palacin –IRAMIS/SPCSI since employment		
2010		Graftfast™ chemistry understanding. Patent filling. Responsibility of contracts with manufacturers. International congress.	
2009		Major actor in the Pegastech setting-up. Patent filling. Responsibility of multipartners contracts. International congress.	
2008		Responsibility of european contracts. PhD management. International congress.	
2007		Major inventor of the GraftFast™ process. Scientific management of the Pegastech start-up. International congress.	
2006		Inventor of the SEEP process. Patent filling.	
2005		Spectroscopic metal/polymer interface signature (XPS and UPS). Patent filling. International congress.	

Initial training*

Dates	
2006	Accreditation to supervise research - Pierre et Marie Curie University (Paris) - : « Polymérisation électro-amorcée à la cathode. Principes et applications. » july 12 2006.
1990	PhD of the Paris VI University : « Etude de l'influence de la structure moléculaire de composés vinyliques sur leur aptitude à former des films de polymère par électropolymérisation sous polarisation cathodique » october 1990.
1987	Master in applied chemistry Pierre et Marie Curie University (Paris)

Additional training (five major)

Dates	
2007	2 training courses : 'how to manage a PhD'
2001-2003	Security training course.
April 99	The management of the professional project
95-96	English training course.
March 1988	Training course, « spectroscopic methods applied to surfaces and interfaces ».



M. DENIAU
Update july 2011

Publications, communications and patents (five major)

Dates	Intitulé et lieu
2006	G. Deniau, L. Azoulay, P. Jégou, G. Le Chevallier and S. Palacin, "Carbon-to-metal bonds : electroreduction of 2-butenenitrile" <i>Surf. Sci.</i> 600, 675 (2006).
2009	Tessier, L.; Deniau, G.; Charleux, B.; Palacin, S. "Surface Electroinitiated Emulsion Polymerization (SEEP): A Mechanistic Approach" <i>Chem. Mater.</i> 2009, 21, 4261-4274.
2010	Mesnage, A.; Esnouf, S.; Jégou, P.; Deniau, G.; Palacin, S. "Understanding the Redox-Induced Polymer Grafting Process: A Dual Surface-Solution Analysis" <i>Chem. Mater.</i> 2010, 22, 6229-6235.
june 2007	Mevellec V., Roussel S., Palacin S., Deniau G., Patent N° 07 55659 « Procédé de préparation d'un film organique à la surface d'un support solide dans des conditions non électrochimiques, support solide ainsi obtenu et kit de préparation »
may 2000	Le Moel, N. Betz, C. Bureau, G. Deniau, C. Baquey, G. Deleris, W. Haberbosch, Patent N° FR 2785812 « Prothèses bioactives, notamment à propriétés immunosuppressives, antisténose et antithrombose, et leur propriétés ».

Other

Language : Anglais

Teaching activity

Surface spectroscopies 1995 to 2003 (≈10h/year).

other activities

Management : 4 PhD, 3 post-docs, 8 masters.

Communication: 5 invited conferences, 6 invited seminars, 18 patents, 35 publications, 12 congress proceedings and book chapters, 25 oral conferences in international congress.

Referee's Actions: reviewer for ACS, Wiley and Elsevier (~15 articles), reviewer in PhD jury.

Awards : winner of the CEA 'idea contest' in 1998. Co-winner of the CEA Technological Innovation Price, 2002.

Major Publications in the field of the invention

1. G. Deniau, G. Lécayon, P. Viel, G. Zalczer, C. Boiziau, G. Hennico and J. Delhalle, " polymer-film formation on the surface of a cathodically polarized nickel electrode in the presence of 4-chlorostyrene " J. Chem. Soc. Perkin Trans. 2, 1433 (1990).
2. G. Deniau, P. Viel, G. Lécayon and J. Delhalle, "UPS and XPS study of the polymer/metal interface of pol(2-methyl-2-propenenitrile) electropolymerized on an oxidized nickel surface cathode" Surf. Int. Anal. 18, 443-447 (1992).
3. G. Deniau, G. Lécayon, P. Viel, G. Hennico and J. Delhalle, "A comparative study of acrylonitrile, 2-butenenitrile, 3-butenenitrile and 2-methyl-2-propenenitrile electropolymerization on a nickel cathode" Langmuir, 8, 267-276 (1992).
4. J. Tanguy, P. Viel, G. Deniau and G. Lécayon, "Study of the grafting and of the electrochemical polymerization of acrylic monomers on a metallic surface by impedance spectroscopy" Electrochem. Acta, 38 (11) 1501 (1993).
5. J. Tanguy, G. Deniau, C. Augé, G. Zalczer, G. Lécayon, "Study of the polymerization mechanisms of methacrylonitrile under cathodic polarization on nickel electrode", J. Electroanal. Chem., 377, 115-123 (1994).
6. E. Léonard-Stibbe, G. Lécayon, G. Deniau, P. Viel, J. Delhalle, " The cationic polymerization of N-Vinyl-2-pyrrolidone initiated electrochemically by anodic polarization on a Pt surface" J. Polym. Science, part A, 32, 1551-1555 (1994).
7. C. Bureau, M. Defranceschi, J. Delhalle, G. Deniau, J. Tanguy, G. Lécayon, " Theoretical monomer/cluster model of a polymer/metal interface : poly(methacrylonitrile) on a nickel surface ", Surf. Sci., 311, 349-359 (1994).
8. C. Bureau, G. Deniau, P. Viel, G. Lécayon, J. Delhalle, " Electrochemistry as a tool to monitor reactions between methacrylonitrile and metallic surfaces: a theoretical and experimental proposal ", J. of Adhesion, 58, 101, (1996).
9. C. Bureau, G. Deniau, F. Valin, M.J. Guittet, G. Lécayon, J. Delhalle, " First attempts at an elucidation of the interface structure resulting from the interaction between methacrylonitrile and platinum anode : an experimental and theoretical (ab initio) study" Surf. Sci. 355, 177, (1996).
10. P. Jonnard, F. Vergand, P. F. Staub, C. Bonnelle
G. Deniau, C. Bureau, P. Viel, G. Lécayon, J. Delhalle, Surf. Int. Anal, 24, 339 (1996).
11. J. Tanguy, G. Deniau, G. Zalczer and G. Lécayon, " Cathodic electropolymerization of methacrylonitrile studied in situ by quartz crystal microbalance, cyclic voltammetry, and impedance spectroscopy "J. Electroanal. Chem., 417, 175-184 (1996).

12. C. Pirlot, J.-C. Bertholet, G. Demortier, J. Delhalle, G. Deniau, P. Viel, F. Valin, G. Lécayon, " Analysis, prior and after exposure to air, of the chemical transformations induced in polyacrylonitrile films by 3 keV proton beams" Nucl. Inst. and methods in physics B, 131, 232, (1997).
13. C. Bureau, G. Deniau, P. Viel, G. Lécayon, *Macromolecules* 30, 333 (1997) comments on " The electroreduction of acrylonitrile : a new insight onto the mechanism" by Mertens et al., *Macromolecules* 29, 4918 (1996).
14. C. Lebrun, G. Deniau, P. Viel, G. Lécayon " Electrosynthesis of poly(4-vinylpyridine) films on metallic surfaces under anodic and cathodic polarizations: structure and properties of the organic coatings" *Surf. and Coating Tech.* 100-101, 474 (1998).
15. G. Deniau, T. Thomé, G. Gaudin, C. Bureau, "Coupled chemistry revisited in the tentative electropolymerization of 2-butenenitrile" *J. Electroanal. Chem.* 451, 145 (1998).
16. G. Deniau, P. Viel, F. Valin, G. Lécayon, C. Pirlot, J. C. Bertholet, G. Demortier, J. Delhalle, "Analysis of the chemical transformation induced at the surface of polyacrylonitrile and polymethacrylonitrile films by 5 keV protons beams" *Nucl. Inst. and methods in physics B*, 151, 109 (1999).
17. P. Viel, C. Bureau, G. Deniau, G. Zalczer and G. Lécayon, "Electropolymerization of methacrylonitrile on a rotating disk electrode at high spinning rate" *J. Electroanal. Chem.* 470 14-22 (1999).
18. G. Deniau, P. Viel, C. Bureau, G. Zalczer P. Lixon and S. Palacin, "Study of the polymers obtained by electroreduction of methacrylonitrile" *J. Electroanal. Chem.* 505 33-43 (2001).
19. C. Pirlot , G. Deniau , P. Viel , G. Lecayon , G. Demortier , J. Delhalle , Z. Mekhalif, "Study of the chemical transformations induced at the surface of bulk iron by protons and alpha beams", *Nucl. Inst. and methods in physics B* 185, 71 (2001).
20. S. Palacin, C. Bureau, J. Charlier, G. Deniau, B. Mouanda and P. Viel, " Molecule-to-metal bonds : electrografting polymers on conducting surfaces " *ChemPhysChem*, 5, 1468, (2004).
21. G. Deniau, J. Charlier, B. Alvado, and S. Palacin; P. Aplincourt and C. Bauvais, "Study of the simultaneous electroinitiated anionic polymerization of vinylic molecules" *J. Electroanal. Chem.* 586 (2006) 62.
22. G. Deniau, L. Azoulay, P. Jégou, G. Le Chevallier and S. Palacin, "Carbon-to-metal bonds: electroreduction of 2-butenenitrile" *Surf. Sci.* 600, 675 (2006).

23. T. Defever, G. Deniau, L. Goux-Capes, S. Barrau, M. Mayne, J.-P. Bourgoïn and S. Palacin
"Cathodic electropolymerization on the surface of carbon nanotubes" J. Electroanal. Chem.
589 (2006) 46-51.

Polymerization reaction coupled to charge transfer: propagation versus termination as a source of permanent travelling waves and multi-peak voltammograms

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Received 6 October 1999; accepted 19 October 1999

Abstract

The voltammetric response for an RRC (radical–radical coupling)-initiated polymerization reaction coupled to an irreversible charge transfer has been considered. Only the propagation and termination steps of the polymeric chains in solution have been taken into account, with the exclusion of any adsorption and hindered diffusion effects. A set of nonlinear partial differential equations is derived. It is demonstrated that this set of equations possesses permanent travelling wave solutions as soon as a newly defined propagation versus termination balance (PTB) parameter γ is greater than unity. These permanent travelling waves feature the building of a uniformly moving polymer/solution boundary as the polymer film is being constructed on the surface under $\gamma > 1$ conditions. Finally, it is found that under $\gamma > 1$ conditions the permanent travelling wave is responsible for the occurrence of a sharp pre-peak on the resulting voltammograms, which is thus directly connected to the abundant consumption of the monomer by the polymerization. All these features are confirmed by a direct numerical resolution of the initial set of nonlinear partial differential equations. The results are in line, qualitatively, with some results which were still uninterpreted, and which were obtained in the electropolymerization of vinylic monomers in anhydrous acetonitrile. In particular, it is demonstrated that the pre-peak can most probably not be assigned either to passivation or to precipitation effects, but is a mere dynamical effect due to the polymerization itself. © 1999 Published by Elsevier Science S.A. All rights reserved.

Keywords: Polymerization reaction; Voltammetry; Charge transfer

1. Introduction

Vinylic monomers such as methacrylonitrile [1], acrylonitrile [2] or 4-vinylpyridine [3] undergo an electropolymerization when submitted to electroreduction at metallic cathodes in an anhydrous organic medium. Two distinct types of polymers are obtained at the end of the synthesis: (i) a physisorbed polymer which can be easily removed by rinsing with a proper solvent (e.g. acetonitrile for polymethacrylonitrile, dimethylformamide for polyacrylonitrile...) [4], and which can be up to several micrometers thick [1] depending on the potential scanning protocol during the synthesis; and (ii) a so-called ‘grafted’ polymer, which is not removed from the metallic surface by rinsing, even under sonication, and which is never thicker than a few hundred angstroms [5].

Even though the two types of polymers (i.e. the grafted and the non-grafted polymer) can be rather easily separated and characterized experimentally [1,5–9], and even though a detailed mechanism has been proposed to account for the formation of the non-grafted polymer (Fig. 1) [10], the voltammograms accompanying the electropolymerization of vinylic monomers at intermediate to large concentrations, have so far resisted satisfactory interpretation, even on a qualitative basis.

The aim of the present paper is to attract attention to theoretical results obtained via a direct modeling of an electropolymerization reaction. The relevance of the model lies in the fact that it makes use only of what is known with some degree of certainty, namely the mechanism for the polymer formed in solution (Fig. 1) [10], in which an RRC (radical–radical coupling)-initiated polymerization is coupled to an irreversible charge transfer. This model suggests that the key parameters in the correct understanding of the voltammograms ac-

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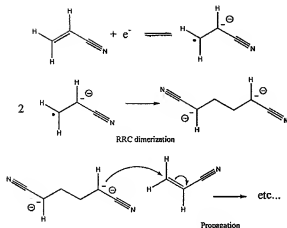


Fig. 1. Mechanism for the formation of a non-grafted polymer.

companying electropolymerization reactions are to be found in phenomena occurring in solution. In this respect, it is thought that the results of the present theoretical model could well orient later experimental testing in new directions.

2. Voltammetric responses in electropolymerization reactions: a brief review

The purpose of this section is to recall some of the unusual features of the voltammograms obtained in electropolymerization reactions, as well as the corre-

sponding interpretations that have been proposed so far in the literature. Not all of the experimental conditions, variants and differences are recalled, and the interested reader is referred to the original publications for detailed experimental information. This brief review is also used to delineate a list of qualitative experimental features which will be compared with the theoretical results of the present model.

For concentrations in acrylonitrile higher than about $5 \times 10^{-2} \text{ mol dm}^{-3}$ in anhydrous acetonitrile, strange multi-peak voltammograms are obtained (Fig. 2) [13,14], while the system involves only one charge transfer step, namely that corresponding to the electroreduction of the monomer. Additionally, this multi-peak regime is absent for concentrations of acrylonitrile in acetonitrile lower than $10^{-2} \text{ mol dm}^{-3}$ or higher than $10^{-1} \text{ mol dm}^{-3}$ [13,14]. The same type of behavior has also been identified with methyl methacrylate at concentrations of the order of $10^{-2} \text{ mol dm}^{-3}$ in anhydrous acetonitrile, as well as in dimethylsulfoxide [17].

For methacrylonitrile, a two-peak regime is also detected at moderate and large concentrations (Fig. 3) [15]. This double-peak regime is absent for concentrations lower than 90% (v/v) in anhydrous acetonitrile [16].

The voltammograms shown in Fig. 3 have been obtained with pure methacrylonitrile (+ tetraethyl ammonium perchlorate as the supporting electrolyte), while those of Fig. 2 have been obtained in a $5 \times 10^{-2} \text{ mol dm}^{-3}$ solution of acrylonitrile in acetonitrile, with the same supporting electrolyte used at the same con-

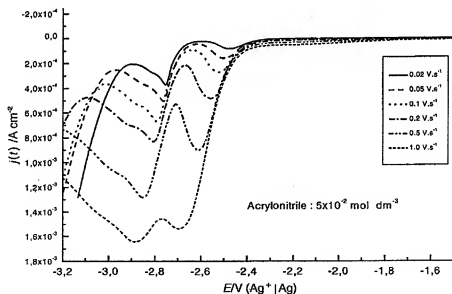


Fig. 2. Experimental voltammograms for the electroreduction of acrylonitrile, $5 \times 10^{-2} \text{ M}$ in acetonitrile + TEAP, for scan rates ranging from 0.02 to $1.0 \text{ V decade}^{-1}$.

centration. The surface area of the electrodes used in both cases is the same, and yet the current densities for methacrylonitrile (Fig. 3) are smaller than those for acrylonitrile (Fig. 2) at the same scanning rate, while one would expect the reverse situation, at least by several orders of magnitude. This comparison is all the more surprising as acrylonitrile and methacrylonitrile differ only by a methyl group, and have standard potentials separated by less than 100 mV.

Initially, the pre-peak observed with acrylonitrile was tentatively attributed to adsorption phenomena [15], in the spirit of the work of Wopschall and Shain [18]. Even though it was noted that this pre-peak has an intensity varying roughly as v (where v is the voltammetric scan rate), no direct cross-check of this proposal could be put forth.

Mertens et al. later suggested that this first peak was due to the grafting reaction itself [19], through a radical initiation of the surface polymerization, although their essential result was that the grafted polymer is present at the potential of the first peak [16]. Actually, there was no evidence that the grafting reaction is the cause of the peak. Moreover, it was later proved that as far as the grafting step and the occurrence of the voltammetric current are correlated, the initiation cannot be anything but ionic [9].

Tanguy et al. were the first to make an *in situ* study of the electropolymerization of methacrylonitrile, by combining electrochemical quartz crystal microbalance (EQCM) techniques, cyclic voltammetry and impedance spectroscopy [20]. Relying on the fact that a significant increase of the eigenfrequency of the EQCM occurs after the peak maximum, it was concluded that the voltammetric pre-peak is a clue to the sudden precipitation of the polymer formed in solution as it reaches its saturation concentration in the vicinity of the surface. It was proposed that this interpretation could well account for the sharp nature of the pre-peaks, as well as their 'clear-cut' asymmetry, the electrode being sud-

denly blocked by the precipitated polymer [21]. In this interpretation, the second peak was obtained thanks to a 'relaxation' of the system, i.e. either via a desorption of the polymer, or via a re-swelling of the polymer by the solvent + monomer mixture, or via a combination of both [20,21].

One drawback of this proposal was that acetonitrile is known to be a good solvent of polymethacrylonitrile, while it is capable only of swelling polyacrylonitrile. In this respect, one would expect the relaxation to be more significant for methacrylonitrile than for acrylonitrile, and hence that a second peak of higher relative intensity would be obtained for methacrylonitrile than for acrylonitrile, while the opposite is found experimentally (Figs. 2 and 3). In addition, recent results have shown that much of the response of the EQCM is actually due to viscosity effects rather than to true mass changes [22], and that the precipitation hypothesis does not hold [23].

From this brief review, it is apparent that one common point of these interpretations is that they all try to interpret the grafting reaction itself: since the most obvious deviation with respect to standard behavior is the occurrence of the double-peak regime (and in particular of the so-called pre-peak) in the voltammograms, this latter feature has been implicitly attributed — or thought to be attributable — to the grafting reaction. However, apart from a detection in the products of reaction [1,5,8], the formation of the grafted polymer — as well as the reactions leading to it — has so far never been evidenced *in situ*.

Double peak voltammograms have already been encountered in the literature [24]. However, in most known cases, the system under consideration is such that two (or more) species are electroactive in the electrochemical medium. The advent of two (or more) peaks is thus to be expected under proper conditions of concentration and/or scan rate. In the present case, only the monomer is electroactive, at least for acrylonitrile and methacrylonitrile. For methyl methacrylate, the polymer is also electroactive in the electrolytic medium, but at a potential which is more negative than that of the monomer by ca. 700 mV, while — in the double peak regime — a pre-peak is obtained [17].

A double peak regime has also been evidenced and accounted for in the case of a catalytic mechanism [25–27]. Even though two redox couples also come into play in this mechanism (one involving the substrate, and one involving the catalyst), only one electroactive species (the catalyst) is actually involved at the electrode surface. However, the double-peak regime can appear only in the catalytic mechanism (in the total catalysis or KT domain [25]) because the charge transfer step is reversible. One additional striking feature of the present mechanism (involving the coupled polymer-

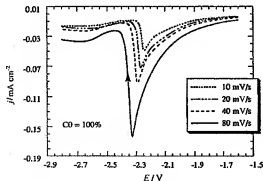


Fig. 3. Experimental voltammograms for the electroreduction of pure methacrylonitrile + TEAP, for scan rates ranging from 0.01 to 0.08 V decade⁻¹.

ization) is that the double-peak regime does exist, even though the charge-transfer reaction and all coupled chemical reactions are irreversible. In addition, for the catalytic mechanism, both peaks have a current varying with the square root of the scan rate, which is not true for our present systems. Finally, in the same catalytic mechanism, both peaks have a current depending linearly on the concentration of the substrate (the equivalent of our monomer), which is far different from our experimental finding that the current of our peaks decrease as a function of concentration.

In the following section, we present a theoretical model in which only a homogeneous polymerization reaction is coupled to the charge transfer, as this is the only information for which direct proof is available [10]. Besides the fact that such a model has never been considered under voltammetric conditions, the purpose is to examine its outcome with respect to: (i) the observation of double-peak regimes; (ii) the range of concentration over which this may be obtained; (iii) the fact that the current of the two peaks varies differently as a function of scan rate; (iv) both peaks have a current decreasing as a function of concentration.

All of these comparison indices are rather qualitative. However, as mentioned in Section 1, the model in itself is probably too preliminary for quantitative comparisons to be relevant. Subsequent sections show that it is nonetheless quite informative, suggesting that the removal of some of the approximations undertaken here and there constitute refinements, which should be performed when a quantitative comparison is under consideration.

3. Model mechanism for the coupled polymerization

3.1. Chemical mechanism

As mentioned above, the accepted mechanism occurring in solution is that of an RRC-initiated polymerization [10]:



where $M^{\bullet-}$ is the product of reduction of the monomer M (the radical anion), $M_2^{\bullet-}$ is the di-anionic dimer formed via the RRC step (Eq. (3.2)), and $M_2^{\bullet-}$ is a di-anionic propagating chain bearing n monomers ($n \geq 2$). We make the traditional approximation that the rate constant k_p for the propagation step (Eq. (3.3)) does not depend on the length of the chain bearing the nucleophilic center. We next consider that the polymerization is anionic, and may thus be terminated by protons ($n \geq 2$):



In Eqs. (3.1)–(3.6), all chemical species are considered in solution, and the adsorption of any of them on the electrode surface is neglected. In addition, we consider that protons responsible for chain termination are static species, i.e. that their concentration is locally time- and space-independent. We return to this same approximation in Section 8.

In the following subsection, the governing partial differential equations corresponding to this problem are derived, and an analytical manipulation is carried out. The purpose is to show, without entering explicitly into the analytical resolution of the equations, that some strange types of solutions may be obtained under certain initial experimental conditions, corresponding to the formation of concentration waves moving away from the surface.

3.2. Governing partial differential equations

Relying on the mechanism described in Eqs. (3.1)–(3.6), the dynamic evolution of the system is governed by the following set of dimensional partial differential equations:

$$\frac{\partial[M]}{\partial t} = D_M \frac{\partial^2[M]}{\partial x^2} - k_p[M] \sum_{i=2}^{\infty} \{[M_i^{\bullet-}] + [M_iH^-]\} \quad (3.7)$$

$$\frac{\partial[M^{\bullet-}]}{\partial t} = D_M \frac{\partial^2[M^{\bullet-}]}{\partial x^2} - 2k_d[M^{\bullet-}]^2 \quad (3.8)$$

$$\begin{aligned} \frac{\partial[M_2^{\bullet-}]}{\partial t} = & D_{M_2} \frac{\partial^2[M_2^{\bullet-}]}{\partial x^2} + k_d[M^{\bullet-}]^2 - k_p[M][M_2^{\bullet-}] \\ & - k_t[M_2^{\bullet-}][H^+] \end{aligned} \quad (3.9)$$

$$\frac{\partial[M_2^{\bullet-}]}{\partial t} = D_{M_2} \frac{\partial^2[M_2^{\bullet-}]}{\partial x^2} - k_p[M][M_2^{\bullet-}] - k_t[M_2^{\bullet-}][H^+] \quad (3.10)$$

$$\begin{aligned} \frac{\partial[M_nH^-]}{\partial t} = & D_{M_nH} \frac{\partial^2[M_nH^-]}{\partial x^2} - k_p[M][M_nH^-] \\ & - k_t[M_nH^-][H^+] \end{aligned} \quad (3.11)$$

$$\frac{\partial[M_nH_2]}{\partial t} = D_{M_nH_2} \frac{\partial^2[M_nH_2]}{\partial x^2} + k_t[M_nH^-][H^+] \quad (3.12)$$

Note that the above set of partial differential equations is infinite, since Eqs. (3.10)–(3.12) are written for every $n > 2$. In the spirit of the work of Needham and co-workers [28,29] and of Bhadani et al. [10], the infinite sums can be avoided by focusing on the global concentration of propagating chains. For this purpose, the following notation is introduced:

$$[P_2^-] = \sum_{i=2}^{\infty} [M_i^-] \quad (3.13)$$

$$[P_1^-] = \sum_{i=1}^{\infty} [M_i H^-] \quad (3.14)$$

$$[P_0] = \sum_{i=0}^{\infty} [M_i H_2] \quad (3.15)$$

In Eqs. (3.13)–(3.15), $[P_0]$, $[P_1^-]$ and $[P_2^-]$ are thus the concentrations of all polymeric chains — regardless of their size — containing zero, one and two active (i.e. anionic) extremities, respectively. In particular, $[P_0]$ is the volumic concentration of the true (saturated) polymer. Assuming that the diffusion coefficients are equal for all species ($=D$), the infinite set of partial differential equations may be reduced to a finite set of partial differential equations:

$$\frac{\partial m}{\partial \tau} = \frac{\partial^2 m}{\partial y^2} - \lambda_p m (\pi_1 + \pi_2) \quad (3.16)$$

$$\frac{\partial m'}{\partial \tau} = \frac{\partial^2 m'}{\partial y^2} - 2\lambda_d m'^2 \quad (3.17)$$

$$\frac{\partial \pi_2}{\partial \tau} = \frac{\partial^2 \pi_2}{\partial y^2} + \lambda_d m'^2 + \pi_2 (\lambda_p m - \lambda_i h) \quad (3.18)$$

$$\frac{\partial \pi_1}{\partial \tau} = \frac{\partial^2 \pi_1}{\partial y^2} + \pi_1 (\lambda_p m - \lambda_i h) + \lambda_i h \pi_2 \quad (3.19)$$

$$\frac{\partial \pi_0}{\partial \tau} = \frac{\partial^2 \pi_0}{\partial y^2} + \lambda_i h \pi_1 \quad (3.20)$$

where the notations and adimensionalizations are identical to those introduced previously by Savéant and co-workers [11,12]: $\tau = Fvt/RT$ is the dimensionless time variable, $y = x(Fv/RTD)^{1/2}$ is the dimensionless space variable. In addition, m , m' , π_2 , π_1 and π_0 refer to the adimensional concentrations in M , M'^- , all di-anionic propagating chains, all mono-anionic propagating chains and all neutral polymer chains, respectively:

$$m = \frac{[M]}{c_M^0}, \quad m' = \frac{[M'^-]}{c_M^0}, \quad \pi_2 = \frac{[P_2^-]}{c_M^0}, \quad \pi_1 = \frac{[P_1^-]}{c_M^0},$$

$$\pi_0 = \frac{[P_0]}{c_M^0} \quad (3.21)$$

where c_M^0 is the initial monomer concentration. The adimensional rate constants, λ_j ($j = d, p$ or i), are defined as:

$$\lambda_j = k_j c_M^0 \frac{RT}{Fv} \quad (3.22)$$

where v is the scan rate of the voltammetric experiment.

The assumption that all diffusion coefficients are equal, though traditional in theoretical electrochemistry, requires a few comments in the present case, as we are dealing with the formation of polymeric chains within the solution. As mentioned in the previous sec-

tion, double peak regimes are often encountered at low concentration (except for methacrylonitrile). Recent experiments have shown that the polymeric chains are remarkably monodisperse, with a degree of polymerization of the order of 10^3 [16]. Thus, if one supposes that the solution has an initial concentration of the order of 10^{-2} mol dm $^{-3}$, and that all monomers are consumed in the polymerization reaction, the overall concentration in polymeric chains should not exceed 10^{-2} mol dm $^{-3}$. The diffusion coefficients D of both the monomers and the polymeric chains (self-diffusion) of mass M , in a solution where the concentration of chains is c may be estimated to behave as $D \sim D_0 \exp(-Mc^u)$, where γ and u are scaling parameters of the order of 0.9 [30]. One thus finds that the expected reduction in the apparent diffusion coefficients because of hindered diffusion effects is of the order of 2%. Apart from local effects, where the concentration in polymeric chains may be higher than the above figures, this is small enough for hindered diffusion effects to be set apart for the moment. We shall, however, return to this approximation in Section 8.

The set of initial and boundary conditions accompanying Eqs. (3.16)–(3.20) is:

$$m(y, 0) = 1; \quad m(+\infty, \tau) = 1 \quad (3.23)$$

$$m'(y, 0) = 0; \quad m'(+\infty, \tau) = 0 \quad (3.24)$$

$$j = 0, 1, 2: \quad \pi_j(y, 0) = 0; \quad \pi_j(+\infty, \tau) = 0 \quad (3.25)$$

$$\Psi = \left[\frac{\partial m}{\partial y} \right]_{y=0} = \Delta m \exp(\alpha \xi) \quad (3.26)$$

$$\xi = -\frac{F}{RT}(E - E^0) = \frac{F}{RT}vt - u, \quad u = \frac{F}{RT}(E_1 - E^0) \quad (3.27)$$

$$\left[\frac{\partial m}{\partial y} \right]_{y=0} + \left[\frac{\partial m'}{\partial y} \right]_{y=0} = 0 \quad (3.28)$$

$$\left[\frac{\partial \pi_j}{\partial y} \right]_{y=0} = 0 \quad (3.29)$$

where E^0 is the standard redox potential of the (M/M'^-) couple, E_1 is the starting potential of the voltammetric experiment, Δ is the adimensional rate constant of the irreversible charge transfer ($=k_0(DRv/RT)^{-1/2}$), α is the charge transfer parameter, and Ψ is the adimensional current, defined as:

$$\Psi = \frac{I}{FSc_M^0 D^{1/2} \left(\frac{F}{RT} \right)^{1/2} v^{1/2}} \quad (3.30)$$

Note that the voltammetric current is conventionally taken as positive for a negative sweep. We have carried out hereafter a direct numerical solution of Eqs. (3.16)–(3.30). However, as described in Section 4, much knowledge may be gained on the nature of the physical

parameters governing the shape of the resulting voltammograms by examining long-time solutions of the set of governing equations. The following section is thus devoted to mathematical manipulation of the set of Eqs. (3.16)–(3.20). No analytical resolution is attempted, but it is shown that peculiar permanent travelling wave solutions can be obtained when the set of input parameters (namely the rate constants and the initial concentrations) fulfil some requirements. These solutions feature the building of concentration waves corresponding to a polymer front moving towards the solution, away from the surface.

4. Permanent travelling waves as solutions

4.1. Conditions for obtaining such solutions: propagation versus termination balance parameter

The set of partial differential equations (Eqs. (3.16)–(3.20)) obtained in the previous section turns out to be strictly equivalent to a modeling of the polymerization process in terms of an autocatalytic procedure [28,29,31–33], in which steps (Eq. (3.3)) and (Eq. (3.5)) of the reaction mechanism may be written formally as:



Such equations are encountered in various models, such as those describing the advance of an advantageous gene, laminar flame propagation, neurophysiology and polymer propagation in industrial reactors [28,29,31–33]. Kolmogorov et al. showed that this type of system possesses travelling wave solutions, which propagate with a uniform velocity [34]. Merkin and Needham have outlined that a proper linearization near the wave front — for small concentrations of products (here P_0 , P_1 and P_2) — of the set of nonlinear partial differential equations enables one to extract necessary conditions for these travelling wave solutions to exist [29]. Let us consider that the concentration of all polymeric materials is small, and that the concentration in monomer is close to its boundary value (Eq. (3.23)), i.e.:

$$m = 1 + \alpha_0 M_0(y, \tau) \quad (4.3)$$

$$m' = \alpha_0 M_1(y, \tau) \quad (4.4)$$

$$\pi_0 = \alpha_0 \Pi_0(y, \tau) \quad (4.5)$$

$$\pi_1 = \alpha_0 \Pi_1(y, \tau) \quad (4.6)$$

$$\pi_2 = \alpha_0 \Pi_2(y, \tau) \quad (4.7)$$

where α_0 is considered as an infinitesimal. Inserting Eqs. (4.3)–(4.7) into the original nonlinear set (Eqs. (3.16)–

(3.20)), and keeping at most terms of order α_0 , leads to:

$$\frac{\partial M_0}{\partial \tau} = \frac{\partial^2 M_0}{\partial y^2} - \lambda_p(\Pi_1 + \Pi_2) \quad (4.8)$$

$$\frac{\partial M_1}{\partial \tau} = \frac{\partial^2 M_1}{\partial y^2} \quad (4.9)$$

$$\frac{\partial \Pi_0}{\partial \tau} = \frac{\partial^2 \Pi_0}{\partial y^2} + \lambda_i h \Pi_1 \quad (4.10)$$

$$\frac{\partial \Pi_1}{\partial \tau} = \frac{\partial^2 \Pi_1}{\partial y^2} + (\lambda_p - \lambda_i h)\Pi_1 + \lambda_i h \Pi_2 \quad (4.11)$$

$$\frac{\partial \Pi_2}{\partial \tau} = \frac{\partial^2 \Pi_2}{\partial y^2} + (\lambda_p - \lambda_i h)\Pi_2 \quad (4.12)$$

Let us now suppose that this system actually has permanent travelling wave solutions, i.e. that it has a nonnegative nontrivial solution which depends only upon the single variable:

$$z = y - \sigma(\tau) \quad (4.13)$$

where $\sigma(\tau)$ is the position of the wave front [28]. The $z < 0$ domain describes the region spatially located before the wave (i.e. where it has already passed), while the $z > 0$ domain is that in front of the wave, where it has not passed. In this respect, Eqs. (4.8)–(4.12) are valid around the wave front ($z = 0$), where — as is described below — there is ideally little polymer formed and little monomer consumed at $z = 0^+$.

Using the transformation (Eq. (4.13)), Eqs. (4.8)–(4.12) can be arranged into a linear set of second-order differential equations:

$$\frac{d^2 M_0}{dz^2} + v \frac{dM_0}{dz} - \lambda_p(\Pi_1 + \Pi_2) = 0 \quad (4.14)$$

$$\frac{d^2 M_1}{dz^2} + v \frac{dM_1}{dz} = 0 \quad (4.15)$$

$$\frac{d^2 \Pi_0}{dz^2} + v \frac{d\Pi_0}{dz} - \lambda_i h \Pi_1 = 0 \quad (4.16)$$

$$\frac{d^2 \Pi_1}{dz^2} + v \frac{d\Pi_1}{dz} + (\lambda_p - \lambda_i h)\Pi_1 - \lambda_i h \Pi_2 = 0 \quad (4.17)$$

$$\frac{d^2 \Pi_2}{dz^2} + v \frac{d\Pi_2}{dz} + (\lambda_p - \lambda_i h)\Pi_2 = 0 \quad (4.18)$$

where $v = d\sigma(\tau)/d\tau$ is the velocity of the permanent travelling wave. Since we are dealing with presumed permanent travelling wave solutions, all concentrations are supposed to depend on z only. In particular, Π_2 , $d\Pi_2/dz$, and $d^2\Pi_2/dz^2$ all depend on z only. From Eq. (4.18), one thus finds that v cannot depend on τ , and is thus a constant. As a consequence, one sees that σ is a linear function of τ , and describes a uniform displacement for the wave front: $\sigma(\tau) = v\tau + \sigma_0$. It is easily seen

that the above set can be solved once Eq. (4.18) is solved, i.e. once $\Pi_2(x)$ is known, so that our focus now turns to Eq. (4.18) alone.

Meaningful solutions of Eq. (4.18) can be obtained only as long as:

$$v^2 - 4(\lambda_p - \lambda_t h) \geq 0 \quad (4.19)$$

i.e.:

$$v \geq 2\sqrt{\lambda_p - \lambda_t h} \quad (4.20)$$

For $v < 2\sqrt{\lambda_p - \lambda_t h}$, the solution is damped oscillatory, giving rise to physically unacceptable negative values for Π_2 . Hence, as in other autocatalytic situations [28,29,31–33], a minimum velocity emerges, which does not depend on the diffusion of the reacting species, but only on the kinetic rate constants of the reaction mechanism. Eq. (4.20) constitutes a necessary, though not sufficient, condition for a complete solution to be found. However, it is straightforward to see that this condition is also sufficient for the system (Eqs. (4.14)–(4.18)) to be solved.

One should note that condition (4.20) can be obtained only if:

$$\lambda_p - \lambda_t h > 0 \quad (4.21)$$

the situation corresponding to a trivial solution which is excluded from the present study. Written in dimensional form, Eq. (4.21) reads:

$$\gamma \equiv \frac{k_p c_M^0}{k_t [H^+]_0} > 1 \quad (4.22)$$

where we define a propagation versus termination balance (PTB) parameter γ .

Our result is, thus, that permanent travelling wave solutions can be obtained as soon as the initial propagation rate is higher than the initial termination rate. Conversely, non-propagating solutions are obtained when $\gamma \leq 1$, when the rate of termination overcomes that of the initial propagation. It is thus clear that the production of polymer in electropolymerization reactions is triggered by the value of γ , and we shall derive our numerical resolutions accordingly.

4.2. Voltammetric shapes under $\gamma > 1$ conditions

Before entering into the numerical resolution of Eqs. (3.16)–(3.20), some additional information may be gathered from the general properties of permanent travelling waves. Some of this deals with the residual concentration $m_t(v)$ of the unreacted monomer behind the wave front [28]. This residual concentration varies with the actual velocity v of the wave and is not strictly zero (see, e.g. figure 3 in Ref. [29], or figure 2 in Ref. [28]). Imagine a situation in which the electropolymerization reaction starts under $\gamma > 1$ conditions, then the abundant polymerization leads to a fast consumption of the monomer, and hence a strong depletion in M close to

the surface (since the initiators are the radical anions created via the charge transfer). Once the permanent travelling wave has been produced, a constant residual — but non-zero — concentration of M remains present behind the wave front, and in particular in the vicinity of the electrode. Indeed, locally, propagation reactions overcome termination reactions as long as:

$$\Gamma(y, \tau) \equiv \frac{k_p c_M(y, \tau)}{k_t [H^+]_0} > 1 \quad (4.23)$$

For a given $\gamma > 1$, if propagation and termination (k_p, k_t) are fast towards both diffusion and charge transfer, then the threshold concentration in M below which the depletion ceases is determined by Eq. (4.23). As soon as $\Gamma(y, \tau) \leq 1$, termination reactions are the dominant process, and the monomer concentration stops decreasing. Chemically speaking, the polymerization kills itself at the electrode because the residual monomer concentration is too low for the propagation to overcome the termination anymore. A residual concentration of the order of:

$$c_M^*(y, \tau) = \frac{k_t [H^+]_0}{k_p} = \frac{c_M^0}{\gamma} \quad (4.24)$$

is thus left behind the wave. One can note that this residual concentration does not depend on y or τ , since it is assumed that the proton concentration is stationary. One thus expects that under conditions in which propagation and termination are fast compared with diffusion and charge transfer, the concentration profile of the monomer has a plateau behind the wave front. One can thus foresee that: (i) the voltammetric current should return to zero and form a first sharp peak and (ii) a second peak is to be expected. As regards the latter, the situation is indeed in many respects identical to the one prevailing at the beginning of the voltammograms, due to the first initial condition in Eq. (3.23), except that this condition is now replaced by:

$$m_t(y, \tau) = \frac{c_M^*(y, \tau)}{c_M^0} \approx \frac{1}{\gamma} \quad (4.25)$$

where $0 \leq y < \sigma(\tau)$, and τ' is a time delay higher than the duration of the induction of the polymerization process (dimerization...etc). Consequently, once the induction is over, once the permanent travelling wave has formed and moved a distance y away from the surface, the concentration profile in the vicinity of the surface right behind the wave front is roughly constant, so that a second voltammetric peak should develop. The conditions under which the charge-transfer reaction restarts is now characterized by a different PTB, which is necessarily less than unity as discussed above. In this way, things happen as if there were no polymerization reaction behind the wave front, and the second peak should have a more or less diffusional shape corresponding to the reduction of the residual monomer

concentration. Should this reasoning be correct, one should observe that this second peak becomes less intense as γ increases, since the intensity of a diffusional peak is proportional to the initial concentration (c_0^0/γ , Eq. (4.24), in the present case). One may note that Eq. (4.25) constitutes an upper boundary to the actual concentration remaining behind the wave, as it supposes that: (i) there is no consumption of the monomer, except via the propagation steps; and (ii) hindered diffusion effects are not considered. We thus expect Eq. (4.25) to be semi-quantitatively valid for moderate γ values at most.

Our present analysis thus suggests that the condition (4.20) should also hold to discuss the occurrence of two peaks on the voltammograms, and that the observation of two peaks on the voltammograms and the production of chemical permanent travelling waves are intimately connected. We shall now illustrate this point on the basis of a numerical resolution of Eqs. (3.16)–(3.20).

5. Numerical scheme and computational details

The set of partial differential equations (Eqs. (3.16)–(3.30)) cannot be solved analytically, and we thus carried out a numerical resolution. This was done using the Elsim software written by Bieniasz [35]. Details regarding this code may be found in Ref. [35] and references therein; however, we merely point out that Eqs. (3.16)–(3.30) have been solved using the Crank–Nicolson implicit finite difference numerical scheme [36], with an dimensional time-step $\delta t = 0.01$ and an dimensional space-interval $\delta y = 0.48$. In most cases, the integration along the time axis is carried out over 4800 grid points with an estimated accuracy of 10^{-4} on the computed dimensional current. The boundary conditions at the electrode ($y = 0$) are solved using the generalized secant method with an initial step factor of 0.1 while the gradients at the electrode are computed via a fifth order multipoint gradient approximation. A cut-off, or dimensional reaction layer thickness, depending on time, $l(t)$, is introduced on the space axis, above which the various dimensional concentration profiles are explicitly equated to the second set of boundary conditions in Eqs. (3.23)–(3.25). We refer to this region as the l -boundary. We have found that in all cases examined herein, a value of $l(t) = 10\sqrt{t}$ was sufficient. The Crank–Nicolson numerical scheme has been chosen because of its — formally unconditional — stability. Although this last assertion is excessive [37], we have not encountered any chaotic behavior in the course of our numerical resolutions. More work is, however, in progress to examine the numerical reliability of our simulation for quantitative purposes, in particular with the use of adaptive grid methods [38]. A complete

voltammogram is obtained in about 5 min on a Pentium II-450 MHz and the values of the dimensional current are finally kept on a set of N grid points in the time-scale, $\{\Psi_k\}_{1 \leq k \leq N}$. In this study, we have taken $N = 160$. In all calculations, the starting potential E_i for the voltammetric scan was taken as $+20$ V more positive than the standard redox potential E° of the (M/M^{+}) couple. This value is thought to be sufficient for the voltammograms to be independent of this starting potential. In all calculations, the transfer coefficient is taken as $\alpha = 0.5$.

5.1. Input parameters

Numerical values must be assigned to λ_p , λ_d , λ_i , A and h as inputs to solve Eqs. (3.16)–(3.20). To our knowledge, none of these values is available in the case of acrylonitrile or methacrylonitrile in anhydrous acetonitrile. We may only estimate h from residual water measurements obtained using the Karl–Fisher method [1]. Even though our measurements fall below the detection threshold of the apparatus, we roughly evaluate the residual water content at 5×10^{-3} mol dm^{-3} , which corresponds to $h \approx 10^{-3}$. This is the value we use in all our simulations. We have arbitrarily taken $\lambda_d = \lambda_p$. This assumption would need careful checking, as the dimerization and propagation steps most probably do not have, e.g. the same activation energy. This point is discussed elsewhere [39].

We have chosen to scan on various values of λ_p . The value of λ_i is then obtained from that of the PTB parameter under consideration:

$$\gamma = \frac{\lambda_p}{\lambda_i h} \quad (5.1)$$

while a new adimensional parameter ζ is defined to decide on the relative magnitude of A with respect to λ_p :

$$\zeta = \frac{A^2}{\lambda_p} \quad (5.2)$$

Hence, for a given set of γ and ζ parameters, all input data are available once the series of λ_p values is given. We have considered both the voltammetric shapes and concentration profiles for several such sets of data. As mentioned in the Review section, the aim of the present paper is to point out that the interpretation of multipoint voltammograms in electropolymerization reactions, such as those of Figs. 2 and 3, on the basis of a building of permanent travelling waves, is *qualitatively* correct. For this reason, we have restricted our numerical analysis to $\zeta = 1.0$. Our present experience is now that the observations described hereafter do not depend — qualitatively — on the actual value of ζ . The actual value of ζ will become relevant for quantitative purposes only, and in particular once the arbitrary $\lambda_d = \lambda_p$ assumption has been released or checked for.

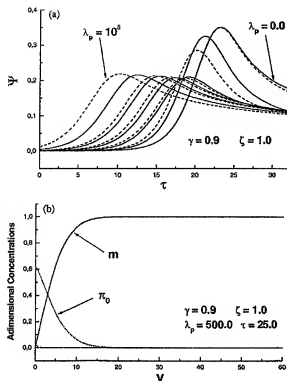


Fig. 4. (a) Simulated adimensional voltammetric current for an RRC polymerization coupled to an irreversible charge transfer, for $\gamma = 0.9$ and $\zeta = 1.0$, $k_d = k_{-d}$, $h = 0.001$ and $\lambda_p = 0.0, 0.1, 0.5, 1.0, 5.0, 10.0, 50.0, 100.0, 500.0, 1000.0, 10000.0, 100000.0$, respectively. (b) Adimensional concentration profiles for an RRC-initiated polymerization coupled to an irreversible charge transfer, for $\gamma = 0.9$, $\zeta = 1.0$, $\lambda_p = 500.0$ and $\tau = 25.0$: m = monomer; π_0 = neutral polymer.

6. Results and discussion

6.1. The $\gamma < 1$ domain and $\gamma = 1$ boundary

Fig. 4(a) shows the adimensional voltammetric current Ψ for $\gamma = 0.9$ and $0.1 \leq \lambda_p \leq 10^5$. It can be seen that each voltammogram bears a single peak, as expected. A transition is observed, roughly between $\lambda_p = 1.0$ and $\lambda_p = 5.0$. This is clearly attributable to the crossing of an intermediate domain separating two kinetic zones, the one at low λ_p probably corresponding to the DO (diffusion only) zone (high scan rate), where diffusion is the rate-limiting step. Apart from this transition, one sees that the peak currents are roughly independent of λ_p in each zone (Fig. 4(a)), implying a dependence of peak current on the square root of scan rate (Eq. (3.30)). Fig. 4(b) shows the corresponding concentration profiles for $\lambda_p = 500.0$ at $\tau = 25.0$: one sees that the concentrations depart from their respective initial values only over a restricted spatial domain, and

in particular that no permanent travelling wave has been built.

Fig. 5(a) shows the adimensional voltammetric cur-

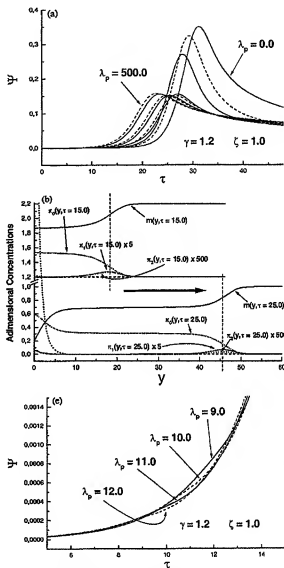


Fig. 5. (a) Simulated adimensional voltammetric current for an RRC polymerization coupled to an irreversible charge transfer, for $\gamma = 1.2$ and $\zeta = 1.0$, $k_d = k_{-d}$, $h = 0.001$ and $\lambda_p = 0.0, 0.1, 0.5, 1.0, 5.0, 10.0, 50.0, 100.0, 500.0$, respectively. (b) Adimensional concentration profiles for an RRC-initiated polymerization coupled to an irreversible charge transfer, for $\gamma = 1.2$, $\zeta = 1.0$, $\lambda_p = 10.0$ and: $\tau = 15.0$ (top), $\tau = 25.0$ (bottom): m = monomer; π_0 = neutral polymer; π_1 = polymer chains bearing one active extremity; π_2 = polymer chains bearing two active extremities. The profiles for each τ value have been shifted for clarity. In each case, the position of the wave front is indicated by a vertical dashed line. (c) Simulated adimensional voltammetric current for an RRC-initiated polymerization coupled to an irreversible charge transfer, for $\gamma = 1.2$ and $\zeta = 1.0$, $k_d = k_{-d}$, $h = 0.001$ and $\lambda_p = 9.0, 10.0, 11.0$ and 12.0 , respectively.

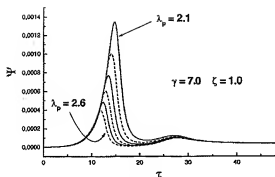


Fig. 7. Adimensional voltammetric current for an RRC polymerization coupled to an irreversible charge transfer, for $\gamma = 7.0$ and $\zeta = 1.0$, $k_d = k_{ps}$, $h = 0.001$ and $\lambda_p = 2.1, 2.2, 2.3, 2.4, 2.5$ and 2.6 , respectively.

6.2. The $\gamma > 1$ domain

The connection between the observation of pre-peaks, and the formation of permanent travelling waves is clearer for higher γ values. Fig. 6(a) shows a series of voltammograms obtained with $\gamma = 3.0$, and Fig. 6(b–e) give the corresponding concentration profiles for the special case where $\lambda_p = 2.6$, at $\tau = 14.6, 15.6, 18.4$ and 30.2 , respectively. These particular values were chosen because they correspond to the beginning of the formation of the permanent travelling wave, the maximum of the first peak, the minimum between the two peaks and the maximum of the second peak, respectively. In Fig. 6(b–d), one sees that while the voltammetric current starts to increase due to the charge-transfer reaction, the polymerization rapidly consumes the monomer in the vicinity of the surface, and soon forces the gradient in M (and hence the current) to go to zero. As described in the previous section, $m(\gamma, \tau)$ then possesses a plateau behind the wave front. As seen in Fig. 6(e), this plateau is further depleted close to the surface because of the — still active — charge-transfer reaction, giving rise to the second voltammetric peak.

An identical analysis of concentration profiles for higher values of γ leads to the same conclusions. As can be seen from Figs. 7 and 8, only the shapes of the voltammetric peaks are dramatically modified. For $\gamma = 7.0$ (Fig. 7), both the pre-peak and the diffusional peak are still observed, the latter being now much less intense than the former, which is pretty much in line both with the discussion of Eq. (4.25), and with the experimental results on methacrylonitrile (Fig. 3). Note that for very high γ values (e.g. $\gamma = 50.0$, Fig. 8), one may come to a point where the diffusional peak is too low to be detected, and the voltammogram bears the sole polymerization peak.

Finally, a direct comparison of the ordinate scales in Fig. 5(a), Fig. 6(a), Fig. 7 and Fig. 8 shows that the range of intensities decreases globally as γ is increased,

and shows that the chemistry coupled to the charge transfer is all the more invisible to electrochemistry as the polymerization is active. This result is in line with what was observed experimentally and has been mentioned in the Review section, namely that the overall intensities on the voltammograms are all the less intense as the concentration in the monomer is high.

7. Preliminary comparisons with experimental facts

As was mentioned in Section 2, the present model contains a certain number of approximations, which probably render it too crude for straightforward quantitative comparisons with experiments to be carried out. This section is thus devoted to a mere comparison with respect to the qualitative experimental indices chosen in Section 2.

1. Appearance of a double-peak regime: as seen in the previous section, double-peak regimes can be obtained on the basis of the present model. This occurs as soon as the PTB parameter γ is larger than 1.

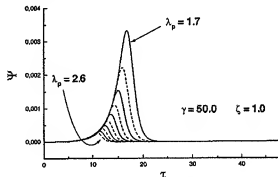


Fig. 8. Adimensional voltammetric current for an RRC polymerization coupled to an irreversible charge transfer, for $\gamma = 50.0$ and $\zeta = 1.0$, $k_d = k_{ps}$, $h = 0.001$ and $\lambda_p = 1.7, 1.8, 1.9, 2.0, 2.1, 2.2, 2.3, 2.4, 2.5$ and 2.6 , respectively.

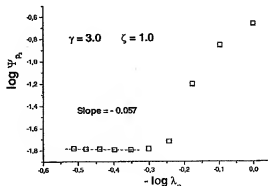


Fig. 9. Log-log plot of the intensity of the diffusional peak (peak 2) as a function of $(1/\lambda_p)$, for $\gamma = 3.0$ and $\zeta = 1.0$.

2. Range of concentration over which the double-peak regime is obtained: from the numerical simulations, the second peak tends to vanish for $\gamma \approx 10$, with the present set of parameters, and an *apparent* single-peak voltammogram is obtained above this value. Since the double-peak regime is impossible for $\gamma < 1$, the present model suggests that the double peak is obtained over a fairly limited range of concentrations, roughly over one order of magnitude. One can note that this is pretty much in line with what is obtained with acrylonitrile or methyl methacrylate.
3. Dependence of peak intensities on scan rate: it was noted previously that the intensities of both the pre-peak and the diffusional peak, e.g. in Fig. 2, have rather unusual dependences on the scan rate. Linear fits in log-log plots reveal that the intensity of peak 1 varies with $v^{0.74}$, while a $v^{0.38}$ dependence is observed for peak 2 (Fig. 2). Our prediction concerning the dependence of the intensity of peak 2, Ψ_{p2} , as a function of the scan rate is contained in Fig. 9. Apart from the transition at high scan rate — already discussed in Section 6.1 — one sees that

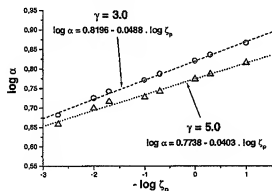


Fig. 10. Log-log plot of the dependence of the intensity of the pre-peak as a function of $-\log \zeta_p$ for $\gamma = 3.0$ and $\gamma = 5.0$. The corresponding linear regressions are given on the figure.

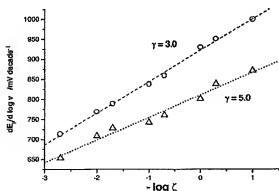


Fig. 11. Peak potential dependence on the scan rate, as a function of $-\log \zeta$, for an RRC-initiated polymerization at $\gamma = 3.0$ and $\gamma = 5.0$.

in the low v domain (corresponding to low values of $-\log \lambda_p$), Ψ_{p2} is almost independent of v . According to the definition of the adimensional voltammetric current, this result indicates that the corresponding dimensional peak should have a dependence very close to $v^{1/2}$, featuring a diffusional behavior. This result is in line with the interpretation of the concentration profiles given in the previous sub-section. A more careful examination however reveals that the log-log plot in Fig. 9 has a slight (-0.057) negative slope, indicating that the actual predicted dependence of Ψ_{p2} on the scan rate is $v^{0.43}$, which is pretty close to the experimental findings. What is actually interesting is that this slight negative slope is present on all the voltammetric series we have examined. Moreover, it has exactly the same numerical value (≈ 0.43), up to a few 10^{-2} , whatever the values of γ or ζ . This particular feature strongly suggests that the origin of the second peak is common to all types of voltammograms, and in particular that this origin is identical in Figs. 2 and 3. This also supports the interpretation given in the previous subsection that this second peak corresponds to the diffusion-limited reduction of the monomer molecules which have not been consumed by the polymerization reaction, and which are left behind the wave. The situation is more involved as regards the v dependence of the first peak, since upon assuming that this dependence is of the form v^γ , it is found that α depends both on γ and ζ (Fig. 10). Typically, the value of α obtained with the parameters of Fig. 6(a) are much too high, of the order of 6 or so. However, as shown in Fig. 10, the dependence of $\log \alpha$ on $\log \zeta$ is linear, and one may thus obtain the value of ζ for a given α once γ is known. The same type of correlation may also be done between $\partial E_{p1}/\partial \log v$ and $\log \zeta$ (Fig. 11), or else between $(E_{p2} - E_{p1})$ and $\log \zeta$, so that both γ and ζ should be obtainable from these cross correlations. One may note that γ may also be obtained from a direct measurement, thanks to the constant current procedure of Bhadani et al. [10], which offers a further confirmation of the predictions. This strategy cannot be used at present, since we have not examined in the present paper a certain number of approximations and assumptions, e.g. $\lambda_d = \lambda_p$, possible hindered diffusion effects, etc. An examination of its influence over the present quantitative predictions is under way, and will be detailed elsewhere [39].

4. Both peaks have an intensity decreasing as a function of concentration: this feature, which is apparent from the experimental voltammograms and has been described in the review section, is nicely reproduced in the present model (compare the range of intensities in Fig. 5(a), Fig. 6(a), Fig. 7 and Fig. 8).

From the present model, the explanation is that the current of the first peak is all the smaller as the consumption of the monomer because of the coupled polymerization is fast, and the latter occurs when the initial monomer concentration is raised. The second peak is due to the electroreduction of the monomer molecules left behind the wave, and this residual concentration is all the smaller as γ is high.

8. Concluding remarks

A mathematical model has been proposed which describes the influence of an RRC-initiated polymerization reaction + termination, coupled to an irreversible charge transfer. The termination reactions are those involving the protonation of the growing anionic chain ends by e.g. residual water and/or other proton sources. Adsorption effects of any type, as well as effects stemming from a possible hindered diffusion of the monomer through a phase containing polymer chains, are not included in the present model. An infinite set of governing partial differential equations is derived from this model. Focusing only on the global concentrations of the growing chains, independently of their size, a finite set of equations is obtained.

An analytical manipulation of this set of equations demonstrates that in the limit of low concentrations of products, it possesses permanent travelling wave solutions, featuring the building of a polymer film via the production of a chemical wave. The first important result of this study is that these permanent travelling waves appear when the ratio γ between the initial propagation ($k_p c_b^0$) and termination ($k_t [H^+]_0$) rates is $\gamma > 1$. The second important result is that the occurrence of these permanent travelling waves is connected with the appearance of two peaks on the resulting voltammograms: a so-called 'pre-peak', caused by the polymerization reaction and the building of the permanent travelling wave, and a diffusional peak stemming from the electroreduction of the residual amount of unreacted monomer left behind the wave front.

On the basis of a numerical resolution of the initial finite set of partial differential equations, these analytical findings are fully confirmed. In particular, it is shown that the overall shape of the voltammogram depends only on the value of γ . Within the present model, a number of qualitative though very unusual features are nicely reproduced, such as: (i) the observation of double-peak regimes; (ii) the fact that this double-peak regime is actually observable only over a fairly limited range of concentration in monomers; (iii) the fact that the second peak is almost of diffusional character, with an intensity varying with v^2 , and $\delta \approx 0.43$, whatever the value of γ or ζ . This value is close to

the experimental findings both for acrylonitrile (0.38) and methacrylonitrile (0.42); (iv) the fact that the intensities of both peaks decrease as a function of concentration.

Another striking result of this model is that it provides such a match with qualitative experimental observations, with so little information. On purpose, only the coupled polymerization is taken into account in addition to diffusion, as it is the only element of the coupled mechanism that is known with certainty for the time being [10]. As regards hindered diffusion effects due to the formation of the polymeric chains within the solution, we have proposed in the present, preliminary, work that this may be set apart, at least for situations in which the double-peak regime is observed at low monomer concentration (acrylonitrile, methyl methacrylate). In that sense, the voltammetric shapes obtained at high values will need further consideration. However, our present experience (to be detailed elsewhere [39]) is that taking hindered diffusion effects into account explicitly in the partial differential equations does not alter the qualitative conclusions: double-peak regimes are obtained, within the same $\gamma > 1$ conditions, and the qualitative criteria examined herein are satisfied. The actual shape of the peaks is modified, with a pre-peak more abrupt and asymmetric than is obtained in the present work.

Finally, we have considered that the concentration of protons is constant. One significant result gained in the series of trials leading to the present paper is that one can *never* obtain two peak voltammograms if this assumption is removed, whatever the concentrations and/or the termination rate constant. In that sense, some of the interpretations provided by the present model need to be questioned. In particular, a practical reason accounting for this buffering has to be put forth. One suggestion is that this buffering is provided by the hydroxides initially present on the (initially oxide-covered) metallic surfaces. Indeed, an oxide surface which has been in the atmosphere of the lab and which is covered with hydroxide groups has a potential of zero charge on the Brønsted scale (the equivalent of the pK_a for a molecule), and that may thus act as a buffer, like any Brønsted acid–base mixing. Moreover, 1 cm² of a surface covered with a hydroxide potentially has 10^{15} protons, i.e. 1.6×10^{-9} mol of protons, to liberate in the 10 ml of our solution, enabling global concentrations of the order of 10^{-7} mol dm⁻³, which is of the order of magnitude of the initial water content. Should this constitute a reservoir coming into play, mostly in the vicinity of the surface, rather high concentrations may be achieved actually leading to a buffer, which may be much stronger than expected. A series of experiments involving a high precision control of the water and hydroxide contents is being carried out to check this hypothesis.

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